

*On a Physical Theory of Stellar Spectra.*

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1. *Introduction.*

The present paper embodies an attempt towards a physical explanation of the ordered gradation in the spectra of stars—a subject in which pioneering work was done by the late Sir Norman Lockyer, but which was worked up with systematic thoroughness at the Harvard College Observatory, under the lead of the late Prof. E. C. Pickering and Miss A. J. Cannon.\* During this interval the spectra of more than 100,000 stars have been photographed, classified, and published with full details in the Henry Draper Memorial Catalogue. The most noteworthy facts which have been brought to light from these monumental studies have thus been summarised by H. N. Russell.†

“The spectra of the stars show remarkably few radical differences in type. More than 99 per cent. of them fall into one or the other of the six great groups which during the classic work of the Harvard College Observatory were recognised as of fundamental importance, and received as designations, by the process of the survival of the fittest, the rather arbitrary letters B, A, F, G, K, M. That there should be so few types is noteworthy, but much more remarkable is the fact that they form a continuous series. Every degree of gradation between the typical spectra denoted by B and A may be found in different stars, and the same is true to the end of the series, a fact recognised in the familiar decimal classification, in which B5A, for example, denotes a spectrum half-way between the typical examples B and A. The series is not merely continuous, it is linear. There exists slight difference between the spectra of different stars of the same spectral class, such as A<sub>0</sub>, but these relate to minor details. Almost all the stars of the small outstanding minority fall into three other classes (or rather four), denoted by the letters P, O, N, R. Of these, O undoubtedly precedes B at the head of the series, while R and N, which grade one into the other, come probably at its other end, though in this case the transition stages are not clearly worked out.”

Russell is of opinion that the principal differences in the stellar spectra arise in the main from variations in a single physical variable in the stellar

\* Harvard, ‘Annals,’ vol. 28, Parts I and II; vols. 56, 76, and 91.

† ‘Nature,’ vol. 93, pp. 227, 252, 281.

atmosphere, and many converging lines of argument show that this variable is the temperature of the stellar atmosphere. Table I shows these facts diagrammatically with provisional values of the temperature.

Table I.

Stellar class.	Typical star.	Secchi's classification.	Temperature.*		Remarks.
			Wilsing and Scheiner.	Saha.	
Pb	The Great Orion Nebula	—	15,000 K†		
Pc	I.C., 4997 .....	—	30,000 K	—	Gaseous nebulae with bright lines.
Oa	B.D. + 35°, 4013...	Type V, including Wolf-Rayet stars.	23,000	23,000–24,000	
Ob	B.D. + 35°, 4001...		—	22,000	
Od	ζPuppis .....				Henceforth all lines are dark.
Oe	29 Canis Majoris				
Oe5	τCanis Majoris ...				
Bo	εOrionis .....	—	20,000	18,000	The sun is a dwarf star of this class.
B5A	γTauri .....	Type I,	14,000	14,000	
Ao	αCanis Majoris ...	Helium and hydrogen stars.	11,000	12,000	
A5F	βTrianguli .....		9,000		
Fo	αCarinae .....	Type II, Yellow-red stars.	7,500	9,000	
F5A	αCanis Minor.....		6,000		
Go	αAurigæ .....		5,000	7,000	
G5K	αReticuli .....		4,500		
Ko	αBootis .....		4,200		
K5M	αTauri .....	Type III, Red stars.	3,200		
Ma	αOrionis .....		3,100	5,000	
Md	0Ceti .....		2,950	4,000	
N	—	Type IV	2,300		
R	—				

\* (Compiled from the Harvard 'Annals,' vol. 91, p. 5, and Russell's paper, *loc. cit.* Temperatures given under the heading Saha are calculated from the method given in the present paper.)

† Buisson and Fabry, 'Journal de Physique,' 1912, p. 472 (calculated according to the limit of interference method).

It is necessary to dwell a little on the physical basis of stellar classification. The earliest astrophysicists classified the stars according to colour; thus Secchi's type I denoted white stars, type II stood for yellow stars, type III for yellow-reddish stars, and type IV for deep red stars. But Lockyer and Pickering found that the varying intensity of particular groups of absorption-lines in stellar spectra was a far better criterion of stellar classification. Table II, compiled from the Harvard 'Annals,' illustrates the principle.

[For the methods by means of which the intensity of a particular line in different stars has been estimated, reference should be made to Harvard 'Annals,' vol. 27, p. 234; vol. 56, p. 56; vol. 91, p. 5. The following is added for the sake of general explanation:—

Numbers which are underlined denote that the line is bright; otherwise

the lines are dark. Lines which are barely visible have the number 1 assigned to them. Faint lines are labelled 2.  $\oplus$  denotes a line of which the intensity cannot be obtained from the Harvard 'Annals.' (?) denotes that the intensity is not stated in numbers in the Harvard 'Annals,' but is compiled from descriptions scattered here and there. The symbol  $M^+$  denotes that the line is due to the ionised atom of the element M, i.e., the atom which has lost one electron. Lockyer called them "proto" elements, and the lines were known as "enhanced lines." We shall subsequently show that they are due to the atom which has lost one electron as the result of the high temperature prevailing in the stars, and acquired a net positive charge.

Table II.—Intensity of Stellar Lines.

Element .....	Helium.		Parhe	He <sup>+</sup>	He <sup>+</sup>	He <sup>+</sup> *	H*	Ca	Ca <sup>+</sup>	Mg <sup>+</sup>
Line .....	4471	4713	4388	4686	4542	4860	4860	4227 (g)	3934 (k)	4481
Series description	2p-4d	2p-4s	2p-5d	3d-4f	4f-9k	4f-8k	2p-4d	1S-2P	1s-2p	3d-4f
Stellar class.										
Pe	—	—	—	$\oplus$	$\oplus$					
Pf	—	—	—	$\oplus$	$\oplus$	$\oplus$				
Oa	0	—	—	$\oplus$	$\oplus$	10				
Ob	0	—	—	100	12		0			
Oc	1	—	—	40	3	3	0	—	—	faint
Od	1	—	—	20	10	20*	10*	—	2	faint
Oe	15	2	3	8	5	25	10	—	2	1
Oe5	15	4	5	5	4	25	20	—	5	1
Bo	15	5	6	2	2	25	25	—	3	2
B2	22	6	10	1	0	35	35	—	4	3
B3	22	6	10	0	0	40	40	—	4	4
B5	10	3	7	—	—	—	60	—	8	7
B8	5	1	3	—	—	—	80	faint	$\oplus$	7 (?)
B9	4	0	1	—	—	—	90	faint	$\oplus$	7
Ao	0	—	0	—	—	—	100	2	10	10
A2	—	—	—	—	—	—	100	4	40	15
A3	—	—	—	—	—	—	90	$\oplus$	70	$\oplus$
A5	—	—	—	—	—	—	70	$\oplus$	80	$\oplus$
Fo	—	—	—	—	—	—	50	$\oplus$	120	$\oplus$
F5	—	—	—	—	—	—	40	15	150 (?)	faint
Go	—	—	—	—	—	—	20	20	200	faint
G5	—	—	—	—	—	—	15	$\oplus$	200 (?)	0
Ko	—	—	—	—	—	—	10	60	150 (?)	0
K5	—	—	—	—	—	—	5	$\oplus$	$\oplus$	
Ma	—	—	—	—	—	—	2	$\oplus$	$\oplus$	
Mb	—	—	—	—	—	—	—	100	faint	
Mc	—	—	—	—	—	—	0	strong	faint	
Md	—	—	—	—	—	—	—	strong	0	

\* The line 4860, generally known as H<sub>β</sub>, has been shown in the Table both as a hydrogen and a He<sup>+</sup> line. For reasons see footnote to Table VII, and the concluding paragraphs of §6.

The Tables show that the lines of an element just appear at a certain stage, rise step by step to a maximum, and disappear at the other end. Thus the He lines just appear at the Ao class, rise to a maximum intensity at the

B3 class, and go out at the Ob class. Similarly for lines of Ca, Mg, H, and groups of nitrogen and oxygen lines not treated here, because their series formulæ are not known.

## 2. *Physical Processes at High Temperatures.*

The explanation of these phenomena follows from the theory of "Thermal Ionisation and Thermal Radiation" of gaseous elements developed by the author in a number of papers published elsewhere. The following is a summary.\*

Up to this time thermodynamics has been confined to the treatment of physical processes like liquefaction and vaporisation, or chemical processes like decomposition or dissociation of molecules into atoms. It has thus carried us up to the stage where all substances are broken up into constituent atoms. But what takes place if a gaseous mass consisting of atoms only be continued to be heated? Hitherto, the ideas on this point have not been very clear. In his interesting theory of internal constitution of stars, Eddington† indeed suggested that in the interior of stars atoms may be, for the most part, broken up into positive nuclei and free electrons—a view which was also supported by Jeans.‡ Following a suggestion by Nernst,§ Eggert|| tried to calculate the temperature required for tearing off the outer ring of eight electrons from the Fe-atom; he was the first to apply Nernst's theorem of the reaction-isochore (which enables us to calculate the chemical equilibrium of a dissociating system from the vapour-pressure data of the products of decomposition), to the above mentioned process of the breaking up of the Fe-atom. But not only is the supposed process a hypothetical one, but also the energy evolved in the process, which is essential for the calculation, was obtained in a rather artificial manner. Lindemann¶ calculated the breaking up of the H-atom into the nucleus and the electron in the solar atmosphere by using a method almost identical with that of the author, and taking the ionisation-potential = 13·6 volts in accordance with Bohr's theory.

The author has shown that the first effect of increasing temperature will be

\* M. N. Saha, "Ionisation in the Solar Chromosphere" (A), 'Phil. Mag.', October, 1920; "Elements in the Sun" (B), December, 1920; "On the Temperature-Radiation of Gases" (C), February, 1921; "On Electron-Chemistry and its Application to Problems of Radiation and Astrophysics" (D), 'Journ. Ind. Ast. Soc.', July, 1920.

† Eddington, 'M.N.R.A.S.', vol. 77, pp. 16 and 596; vol. 79, p. 2.

‡ Jeans, 'M.N.R.A.S.', vol. 79, p. 319.

§ Nernst, 'Die Theoretische und Experimentellen Grundlagen des Neuen Wärme-satzes,' 1918, p. 154, Chap. 13, concluding paragraph.

|| Eggert, 'Phys. Zeit.', December, 1919, p. 570.

¶ Lindemann, 'Phil. Mag.', December, 1919.

to tear off the outermost electron from the atomic system, as represented in the equation,

$$\text{Ca} = \text{Ca}^+ + e - U_1. \quad (1)$$

The energy of ionisation for a gm.-atom can be exactly calculated (*i.e.*, in a way free from any hypothesis about the arrangement of electrons about the nucleus), from the ionisation-potential  $V_i$ , with the aid of the formula,

$$U_1 = \frac{eV_i N}{300J} \text{ calories.} \quad (2)$$

[ $N$  = Avogadro-number,  $J$  = mechanical equivalent of heat.]

In cases where the ionisation-potential is not known from direct experimental work, it can be calculated from the convergence-frequency,  $1s$ , of the principal series of the element with the aid of the quantum relation\*

$$V_i = \frac{h(1s)}{e} \cdot 300 \text{ (in. volts).} \quad (3)$$

There is now very little doubt that the relation is exact. In certain cases the  $1s$ -term is very large, and, as the principal series lie beyond the Schumann region, it has not been obtained at all. In such cases the  $2s$ -term is often mistaken for the  $1s$ -term. Helium is a well-known example. What are usually called the principal series of helium and the so-called par-helium are not  $1s$ - $mp$  series at all, but  $2s$ - $mp$  series.† That this is so clear from the associated property that ordinary cool vapour of helium does not absorb the so-called principal series at all, but is quite transparent to them. If these were the true principal series, helium would have absorbed these lines ( $\lambda = 20587, 10830$ , etc.), just as sodium-vapour absorbs the  $D_1$  and  $D_2$  lines.

Another good example is thallium, discussed by Foote and Mohler 'Phil. Mag.,' vol. 37, p. 33.

At a given temperature and concentration, a definite equilibrium will be established between the proportions of  $\text{Ca}$ ,  $\text{Ca}^+$ , and  $e$ , as represented by the Van't Hoff formula of reversible chemical reaction,



\* This relation, which is fundamental in the theory of the ionisation-potential, has now been definitely established for a number of elements. For a comprehensive account see McLennan, 'Proc. Phys. Soc. Lond.,' December, 1918. Franck and Hertz, 'Phys. Zeit.,' vol. 20, p. 132 (1919). The relation has been definitely established for:—Hg, Franck and Hertz, Davis and Goucher, 'Phys. Rev.,' vol. 10, p. 101 (1917); Na, Cd, Rb, Zn, Tate and Foote, 'Phil. Mag.,' vol. 36, p. 64 (1918); Mg, Tl, Foote and Mohler, 'Phil. Mag.,' vol. 37, p. 33; Rb, As, Cs, Foote, Rognley, Mohler, 'Phys. Rev.,' vol. 10, p. 59; Pb, Ca, Mohler, Foote, Stimson, 'Phil. Mag.,' vol. 40, p. 73; Cs, Foote and Meggers, 'Phil. Mag.,' vol. 40, p. 80.

† *Vide* Franck and Reiche, 'Zeits. f. Physik,' vol. 1, p. 154 (1920).

The equation of the reaction-isochore for calculating the equilibrium is\*

$$\log \frac{x^2}{1-x^2} P = -\frac{U_1}{2.3 RT} + \frac{5}{2} \log T - 6.5. \quad (5)$$

Where  $x$  = fraction ionised,  $P$  = total pressure.

Calculations for the ionisation of Ca, Sr, Ba, Mg, Na, K, Rb, Cs, H, He, will be found in the papers A and B.

The next point in question is the identification of the ionised elements in the physical systems in which they may occur. Spectroscopically,† it is quite an easy matter, for the ionised elements show a system of lines which is quite different from the lines of the neutral atom. They are generally known as “enhanced lines.” The line-system of the neutral atoms, when classified into series, have the Rydberg number  $N = (2\pi^2 e^4 m / h^3)$ , but the enhanced lines can be grouped into series only with the Rydberg number  $4N$ . This fact has been very satisfactorily established for  $\text{He}^+$ , and the alkaline earths by Fowler‡ and Lorensen.§ It is an easy corollary from Bohr’s theory of spectral emission that such lines should be due to the ionised atom.

For Zn, Cd, and Hg, Paschen and Wolff|| have discovered a number of lines in the extreme ultra-violet, which are analogous to the lines of the alkaline earths.¶ Fues shows that these lines are due to the ionised atoms of the elements. For other elements, some lines are supposed to be due to the ionised atom, but these have not yet been grouped into series or critically investigated.\*\*

At the end of § 5, a Table of the chief lines of the neutral and ionised elements are given, with their series-position.

### 3. *Physical Processes Leading to Ionisation—Radiation of the Characteristic Lines of the Neutral Atom.*††

The process of ionisation cannot be an abrupt one, for the electron, in the course of passing off to infinity, can take up an infinite number of stable

\* For the deduction of this formula, see Paper A, *loc. cit.*

† For a *résumé* of the early works to detect ionisation in heated gases, see McLennan, ‘Roy. Soc. Proc.,’ A, vol. 92, p. 591. McLennan’s own experiments with Hg, Zn, Cd, Ti-vapour seems to be quite inconclusive.

‡ Fowler, “Bakerian Lecture,” ‘Phil. Trans.,’ vol. 214.

§ Lorensen, ‘Inaug. Dissertation,’ Tübingen, 1913.

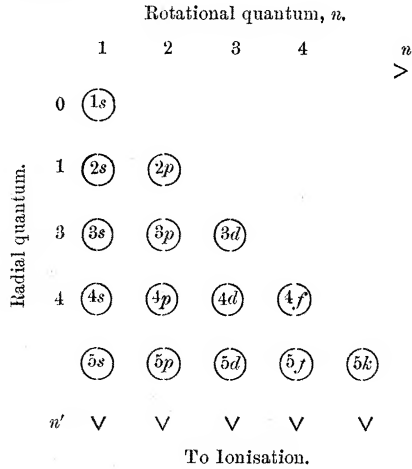
|| Paschen, ‘Ann. der Physik,’ vol. 35 ; Wolff, *loc. cit.*, vol. 42, pp. 825–839.

¶ Fues, ‘Ann. der Physik,’ vol. 63, No. 17 (1920).

\*\* For example, the Grund-Spektra of Alkalies, discussed by Goldstein, ‘Ann. der Physik,’ vol. 27, p. 773 ; Schillinger, ‘Wien. Ber.,’ p. 608, 1909, and Nelthorpe, ‘Astrophysical Journal,’ January, 1915 ; also the enhanced lines discussed by Lockyer and others.

†† See Saha, ‘Phil. Mag.,’ February, 1921, “On the Temperature Radiation of Gases” (C).

orbits characterised by the rotational quantum-number  $n$ , and the radial quantum number  $n'$  [ $n = 1, 2, 3, \dots, n' = 0, 1, 2, \dots$ ], according to the Bohr-Sommerfeld\* theory of spectral emission. The various quasi-stationary orbits are represented in the following diagram, which is a slightly modified form of one given by Bohr.†



In a mass of atoms, comparatively cool, and not subject to any stimulus, the atoms have their vibrating electron in the 1s-orbit. This orbit is circular, corresponding to  $n = 1, n' = 0$ , and has the energy  $A - h(1s)$ . This mass of gas does not emit any light, and when traversed by a continuous beam, can absorb only lines of the principal series,  $\nu = 1s - mp$ .‡ It cannot absorb lines of the diffuse, sharp or fundamental series. But if we continue to heat up the mass, atoms will progress towards ionisation through the quasi-stationary stages represented in the above diagram, and radiation will follow as a result of the mutual interchange of orbits.§ First of all we shall have emission of 1s-2p line or lines (fundamental lines), to be followed by the emission of the 1s-mp series. When the mass of gas emits the line 1s-2p rather strongly it can absorb lines of the sharp or diffuse series.|| At a

\* Sommerfeld, "Atombau und Spektral-Analyse."

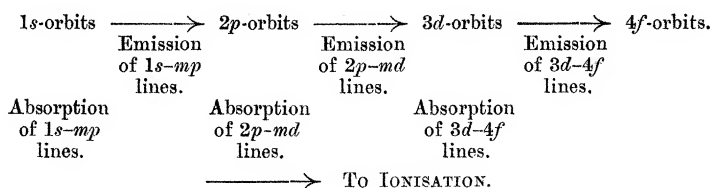
† Bohr, 'Zeitschrift für Physik,' vol. 2, p. 434 (1920).

‡ This fact, which comes out as a necessary corollary of the Bohr-Sommerfeld theory, has been experimentally established for Na-vapour (Wood, 'Astr. Jour.,' vol. 29, p. 97; vol. 43, p. 73); for the other alkalis (Bevan, 'Roy. Soc. Proc.,' A, vol. 83, pp. 821-828; vol. 84, pp. 209-225; vol. 85, pp. 54-76), and Hg (Wood, 'Phys. Zeit.,' vol. 14, pp. 191-195 (1913)), for cadmium (Wood, 'Astr. Jour.,' vol. 29, p. 211).

§ For attempts to apply the quantum-theory to these cases, see the following papers:—Einstein, 'Phys. Zeit.,' 1918, p. 124; Planck, 'Ann. der Physik,' vol. 50; 'Berliner Sitz. Ber.,' 1916; 'Verh. D. Physik. G.,' vol. 17 (1915).

|| As a matter of fact, the 2p-ms lines, as well as the 2p-md lines, have not been reversed at all in the laboratory for any element, when the light is passed through

further stage the  $2p\text{-}md$ , or  $2p\text{-}ms$  lines will begin to be emitted. The gas will now be able to absorb the fundamental series. The whole process can thus be symbolically written :—



The theory is not yet sufficiently perfect to enable us to calculate the proportion of atoms in the quasi-stationary orbits characterised by the quantum numbers  $n$  and  $n'$ , but some general statements can be made.\* The "radiation temperature" (*i.e.*, the temperature at which the fundamental line  $1s\text{-}2p$  is emitted, and  $2p\text{-orbits}$  are just commencing to form) will be higher, the higher is the ionisation-potential of the element. Other orbits will be formed at temperatures intermediate between this and the temperature at which ionisation is completed. At any stage, the proportion of atoms distinguished by the quantum numbers ( $n, n'$ ) will be smaller, the larger are the values of  $n$  and  $n'$ . So that we see that the  $1s\text{-}2p$  line (and  $1s\text{-}mp$  series) will be the first to come out, the last to go, the least amount of element will show them† and will be the most intense line all the while. The  $2p\text{-}md$ ,  $2p\text{-}ms$ ,  $2s\text{-}mp$  lines will come out later, go out earlier, and will be increasingly fainter. The disappearance of  $1s\text{-}2p$  line may be taken as marking the completion of ionisation.

cool vapour (J. J. Thomson, 'Phil. Mag.,' April, 1919). The Balmer series of hydrogen, which may be regarded as the combined sharp and diffuse series of that element, are not reversed when continuous light is passed through ordinary  $H_2$ -vapour; but Ladenburg and Loria ('Verh. der D. Physik. G.,' vol. 10, p. 858 (1908)) showed that they can be obtained as reversed lines when the absorbing column of  $H_2$ -vapour is traversed by an electric current. Similarly, Paschen obtained the reversal of the so-called principal series lines of He and Parhe ( $\lambda = 10830, 20587$ ) by passing an electric current through the absorbing column of helium-gas; ordinary helium-gas is quite transparent to these lines. This shows that the lines are not really principal lines.

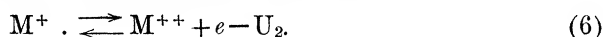
\* Based partly on the works of Planck and Einstein (*loc. cit.*), Planck tries to calculate the distribution of atoms in the different orbits, and Einstein considers the emission and absorption of radiant energy from the standpoint of quantum-statistics. See also Epstein, "Zur Theorie des Starkeffektes," 'Ann. der Physik,' vol. 50, p. 489, who considers the relative probability of passing to the quasi-stationary orbits characterised by the quantum numbers  $n$  and  $n'$ .

† Cf. the experiments of Du Gramont on the "Raies Ultimes" of elements, which are either the  $1s\text{-}2p$  line or such lines of  $1s\text{-}mp$  series as lie in the visible region. Du Gramont, 'Bull. Soc. franç. de Phys.,' 1911, No. 14.

#### 4. Theory of Second-step Ionisation.

Let us now consider what takes place when the first-step ionisation is completed. Suppose that we have a gaseous mass consisting wholly of  $\text{Ca}^+$ -atoms, and we continue to heat it up. It is clear that we shall have the emission of the ionised elements, *i.e.*, of the enhanced lines, followed by the commencement of a second-step ionisation, in which  $\text{Ca}^+$  loses another electron, and acquires a net double positive charge.

The second-step ionisation is represented by the formula



The value of  $U_2$  is generally very large, and have not been at all experimentally investigated. But, in the case of helium and the alkaline earths, the enhanced lines have been completely studied and grouped into series. From this we can calculate the energy of second-step ionisation by applying formula (2).

#### Second-Step Ionisation.\*

Element.	1s.	Ionisation-potential.	$U_2$ in calories.
He .....	4N	53.4 volts.	$12.3 \times 10^5$
Mg .....	121,270	15.02 "	$3.46 \times 10^5$
Ca .....	95,740	11.86 "	$2.70 \times 10^5$
Sr .....	88,840	10.70 "	$2.50 \times 10^5$
Ba .....	80,575	9.86 "	$2.30 \times 10^5$
Zn .....	147,544	18.20 "	$4.18 \times 10^5$
Cd .....	140,226	17.30 "	$3.98 \times 10^5$
Hg .....	161,800 (?)	19.95 "	$4.60 \times 10^5$

Let us suppose that the fractions  $x$  and  $y$  of the total Ca-atoms are dissociated to  $\text{Ca}^+$  and  $\text{Ca}^{++}$ -atoms respectively. Then it can be easily shown that the equation of chemical equilibrium is of the form

$$\log P \frac{x^2}{(1-x-y)(1+x+2y)} = -\frac{U_1}{2.3 RT} + \frac{5}{2} \log T - 6.5, \quad (7)$$

$$\log P \frac{y^2}{x(1+x+2y)} = -\frac{U_2}{2.3 RT} + \frac{5}{2} \log T - 6.5. \quad (8)$$

Since we are confining ourselves to the range where the proportion of

\* Fowler, 'Phil. Trans.,' A, vol. 214; and new calculations not yet published; Fues, 'Ann. d. Physik,' vol. 63, No. 17; Fues's figures for the 1s-terms of  $\text{Zn}^+$  and  $\text{Cd}^+$  are 159,000 and 155,000. The above figures are due to Fowler. The figure for  $\text{Hg}^+$  has been calculated by me by using the interesting relation that the 1s-term of the enhanced series is roughly 17/9 times the 1s-term of the neutral line system in the case of the alkaline earths, and Zn and Cd. *Vide* Fues, *loc. cit.*

neutral Ca-atoms is vanishingly small, we can put  $x+y = 1-\epsilon$ , where  $\epsilon$  is a small fraction. The equation (8) then takes the form

$$\log \frac{Py^2}{(1-y)(2+y)} = -\frac{U_2}{2.3 RT} + \frac{5}{2} \log T - 6.5. \tag{8'}$$

It is no longer necessary to consider equation (7). The following Table shows the percentage of second-step ionisation of the alkaline earths at pressures of 1 and  $10^{-1}$  atms. Percentage of the first-step ionisation is also shown for the sake of comparison.

Table III.

Element temp.	Mg.	Mg <sup>+</sup> .	Ca.	Ca <sup>+</sup> .	Sr.	Sr <sup>+</sup> .	Ba.	Ba <sup>+</sup> .
10,000	56-90	—	85-99	8-26	90-100	14-40	94-100	23-56
11,000	75-96	—	93	18-44	95	26-64	—	40-78
12,000	86-98	—	97	31-70	98	49-89	—	59-91
13,000	93-99	10-35	99	47-86	—	61-92	—	75-96
14,000	96	21-54	—	64-93	—	76-96	—	86
15,000	98	32-72	—	81-97	—	88	—	92
16,000	99	46-85	—	87	—	92	—	96
17,000	—	61-92	—	92	—	96	—	98
18,000	—	74-96	—	95	—	98	—	
19,000	—	83-98	—	99				
20,000	—	89-99	—	99				
21,000	—	93						
22,000	—	96						
23,000	—	98						

In each pair of columns, the first gives the percentage of ionisation under a pressure of 1 atm., the second under a pressure of  $10^{-1}$  atms.

The following Table gives the ionisation of helium (both first-step and second-step) at temperatures higher than 16,000° K.

Table IV.—First-Step Ionisation of Helium.

Pressure temperature.	1	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	Atm.
17,000	9	28	66	94	99	Complete.
18,000	14	41	81	97	—	
19,000	21	57	90	99		
20,000	31	71	95	—		
21,000	41	81	98			
22,000	53	89	99			
23,000	64	93	—			
24,000	73	96				
25,000	81	98				
26,000	87					
27,000	91					
30,000	98					

Table V.—Second-Step Ionisation of Helium.

Pressure temperature.	$10^{-3}$ .	$10^{-4}$ .	$10^{-5}$ .	$10^{-6}$ .
24,000	—	10	24	60
25,000	—	14	39	78
26,000	—	23	57	90
27,000	10	33	72	93
28,000	17	47	86	98
29,000	26	63	95	Complete.
30,000	35	77	97	"

The second-step ionisation of helium is too small even in stars having the highest temperature. Consequently,  $\text{He}^+$  lines should be observed even when the temperature reaches  $40,000^\circ \text{K.}$ , but actually they disappear from the Pc-class of gaseous nebula, the temperature of which is not probably so high. Probably this is an effect of low pressure. According to Emden,\*  $P = 10^{-5}$  atm. in nebulae. This brings the temperature of the completion of the ionisation of  $\text{He}^+$  to  $29,000^\circ\text{--}30,000^\circ \text{K.}$ , which is not improbable.

Table VI gives the ionisation of hydrogen. It will appear from the Tables that hydrogen should definitely disappear when the temperature reaches the value  $22,000^\circ \text{K.}$ , but this is not the case, for, according to the 'Harvard Annals,' the Balmer lines occur not only up to the Oa-class, but also in the Pa-class of nebulae, the temperature of which is probably very large.

Table VI.—Ionisation of Hydrogen.

Pressure temperature.	1-atm.	$10^{-1}$ .	$10^{-2}$ .	$10^{-3}$ .	$10^{-4}$ .	$10^{-5}$ .
7,000	—	—	—	1	4	1.5
7,500	—	—	1	3	8	12
8,000	—	—	2	5	18	26
9,000	—	2	6	20	55	44
10,000	2	5	18	49	86	89
11,000	4	13	39	80	97	
12,000	9	28	68	94		
13,000	16	45	84	98		
14,000	27	65	93			Complete ionisation.
15,000	40	81	97			
16,000	55	90				
17,000	69	94				
18,000	80	97				
19,000	87					
20,000	92					
21,000	95					
22,000	97					
23,000	—					

\* Emden, 'Gaskugeln,' p. 282.

5. Characteristic Lines of Neutral and Ionised Elements.

In § 3 we remarked that the ionised elements have a system of characteristic lines which are quite different from the line-system of the neutral element. Table VII shows the chief lines of both systems side by side for a few elements. Here  $1s\text{--}mp$ ,  $2p\text{--}md$ ,  $2p\text{--}ms$ ,  $3d\text{--}mf$  respectively stand for the principal, the diffuse, the sharp, and the fundamental series. The  $1s$  term is generally single, but the other terms are double, treble, or sometimes quadruple. In the principal series  $m$  begins with 2, in the diffuse with 3, in the sharp with 2, and in the fundamental with 4. Generally the headline of the series, and in some cases the next one or two, are given.

Table VII.

Element.	Principal $1s\text{--}mp$ .	Diffuse $2p\text{--}md$ .	Sharp $2p\text{--}ms$ .	Fundamental $3d\text{--}4f$ .	Remarks.
H .....	1215·3 (etc.).	H <sub>α</sub> 6562·8 H <sub>β</sub> 4861·3 (etc.).	—	18,751	The sharp series coincides with the diffuse series.
He .....	570-480 (?)	5875 4471 6678 4922	7065 4713 7281 5047	? ? —	Helium. So-called parhelium.
He <sup>+</sup> .....	304-278 (?)	1640 1215 1087 (etc.).	—	4686	The sharp series coincides with the diffuse series as in H.
Mg .....	2852·11 4571·38	3838·29 32·31 29·36	5183·62 72·70 67·38		
Mg <sup>+</sup> .....	2795·52 2802·70	2797·99 2790·77	2936·50 2928·63	4481	The 4481 line is also double.
Ca .....	g 4226·73 6572·78				
Ca <sup>+</sup> .....	K 3933·66 H 3968·47	— —	3736·90 06·02		
Sr .....	4607·34				
Sr <sup>+</sup> .....	4077·88 4215·66	— —	4305·60 4161·95		
Ba .....	5535·69				
Ba <sup>+</sup> .....	4554·21 4934·24				
Zn .....	2139·33 3075·99				
Zn <sup>+</sup> .....	2025·57 2061·98	— —	2558·03 2502·11		
Cd .....	2288·79 3261·17				
Cd <sup>+</sup> .....	2144·45 2265·13	— —	2748·68 2573·12		
Hg .....	1849·0 2536·72				
Hg <sup>+</sup> .....	? ?	—	2847·85 2224·70		

The principal series of hydrogen is given by the formula  $\nu = N(1/1^2 - 1/m^2)$ , the combined sharp and diffuse series by  $\nu = N(1/2^2 - 1/m^2)$ , and the fundamental series by  $\nu = N(1/3^2 - 1/m^2)$ . They are usually named after Lyman, Balmer, and Paschen respectively.

The classification given for helium lines is somewhat different from that usually given. The lines 20857, 5016... and 10830, 3889..., which are usually regarded as the principal series of parhelium and helium, are here regarded as  $2s\text{-}mp$  series; for reasons see § 2. The  $1s$ -term is, as Franck remarks,\* probably single, and is calculated from the ionisation-potential 25.4 volts, as experimentally obtained. The head-lines are calculated by taking  $2p$  from the parhelium terms.† Probably 570-480 may be the lines detected photo-electrically by Richardson and Bazonni.‡

The figures for the principal series of  $\text{He}^+$  are calculated from the series formula  $\nu = 4 N(1/1^2 - 1/m^2)$ ; the lines, of course, have not been identified. The combined sharp and diffuse series lines  $\nu = 4 N(1/1^2 - 1/m^2)$  have been obtained by Lyman. The 4686 is the head-line of the Bergmann or "fundamental" combination  $\nu = 4 N(1/3^2 - 1/m^2)$ . The next series combination,  $4f\text{-}mk\text{-}...$ , is represented by the formula  $\nu = 4 N(1/4^2 - 1/m^2)$  and include the Pickering lines  $\nu = N[1/2^2 - 1/(m + \frac{1}{2})^2]$  as its odd members, while the even members reduce to the Balmer formula for hydrogen,  $\nu = N(1/2^2 - 1/m^2)$ . Their wave-lengths are, however, slightly different, owing to slightly different value of  $N$  for  $\text{He}^+$ . The intensity of these lines is also very small.§ The series  $\nu = 4 N(1/3^2 - 1/m^2)$  and  $4 N(1/4^2 - 1/m^2)$  were first obtained in the laboratory by Fowler.||

For the neutral atom of the alkaline earth group and Zn, Cd, Hg the principal lines given are those corresponding to the series combination  $1S\text{-}2P$ ,  $1S\text{-}2p_2$ .¶ These are the most important lines, for experiments on ionisation-potential show that these are the first to come out when the gas is bombarded by electrons possessing the proper quantum-voltage. The ionised atoms show a system of doublets like the alkalis.

The interest of the above Table lies in the fact that it affords a possibility of spectroscopically testing the ionisation produced by a high temperature. For example, let us take a small quantity of calcium, sealed within a quartz tube which is fitted with plane ends, and then begin to heat the tube, and allow a beam of continuous light to pass through the tube. Then as soon as

\* 'Zeits. f. Physik,' vol. 1, p. 154.

† Franck, *loc. cit.*

‡ 'Phil. Mag.,' vol. 34, p. 285 (1917).

§ Evans, 'Phil. Mag.,' vol. 29, p. 284 (1913).

|| 'Phil. Trans.,' vol. 214.

¶ *Vide* Fowler, *loc. cit.*

calcium vapour is formed, the spectrum of the transmitted beam will, on spectroscopic examination, be found to be crossed with the dark absorption lines  $\lambda = 4227$ ,  $\lambda = 6573$ , and other associated lines of the  $1S-mP$ ,  $1S-mp_2$  series. The H, K lines will not be reversed; but if we go on increasing the temperature, then provided that the tube does not collapse, we shall find absorption lines of the diffuse and sharp series lines. Ultimately we shall find the H, K lines as reversal lines. The appearance of these lines may be taken as an indication that a good proportion of Ca atoms has become ionised.

On account of the high value of the ionisation-potential of Ca and the elements given above, it is very doubtful, however, whether experiments described above can succeed with quartz tubes or tubes of similar refractory substances known up to the present time. Experiments with the alkali elements Cs, Rb, K are more likely to succeed, for these have very low ionisation-potentials, but the knowledge of their enhanced lines is very meagre.

In view of the total lack of laboratory data to test our hypothesis, we have to turn to the stellar data given in § 1. This is done in the next section.

#### 6. *Physical Processes taking place in Stars; Temperature of Emission of the Stellar Atmospheres.*

The physical meaning of the appearance and disappearance of lines given in § 1, Table II, now becomes apparent. Let us start with the calcium "g" and  $Ca^+ - K$  lines.

The "g" line appears in maximum intensity from the very stage when the star begins its effective life. There is no trace of the K line at the lowest stages. This just begins to appear at the Mc-stage, showing that calcium has just begun to be ionised. As we go higher up, the ionisation increases (g is fading off, K becoming more intense). The "g" line completely disappears at the B8-stage, showing that here all calcium has been ionised to  $Ca^+$ . The K line reaches a maximum intensity at the G5-stage, then steadily diminishes, showing that a second step ionisation has begun. It disappears completely at the Oc-stage showing that all  $Ca^+$  has been further ionised to  $Ca^{++}$ , from above this stage.

Now referring back to Table III, we can assign the following temperatures to the points of completion of ionisation,

B8.....	Ca completely ionised .....	13,000° (Ca 1·5 p.c.).
Oc .....	$Ca^+$ completely ionised to $Ca^{++}$ .....	20,000° ( $Ca^+$ 1 p.c.).

and we have also at the stages

Mc .....	Ca just begins to be ionised .....	4,000° ( $Ca^+$ just traces).
Go .....	Maximum proportion of Ca-atoms	70,00°.

Both Ca and  $\text{Ca}^+$  can be identified with the aid of their fundamental lines  $1s-2p$ . But such is not the case with any other element excepting Sr,  $\text{Sr}^+$ , Ba, and  $\text{Ba}^+$ , for which we have no satisfactory data. It is well known that owing to atmospheric absorption, observations have to be confined to the spectral region  $\lambda = 3600$  to about  $\lambda = 6000$ . It seems to be generally recognised, but nowhere clearly stated, that this fact alone tends to give decided preference to certain elements to the exclusion of others.

For example, let us take hydrogen. In the stars, it can be identified by the  $2p-md$  lines, the  $1s-mp$  lines falling within the region of atmospheric absorption. But according to § 2, the  $2p-md$  lines cannot be absorbed by the ordinary H-atoms, but by such H-atoms of which the electron is in the  $2p$  orbit. We can have such orbits only at high temperatures. Hence we find the Balmer lines gradually disappearing in the lower stages. We have at the stage

Mb .....  $2p$ -orbits of H just appearing .....  $T = 4500^\circ$ .

On the other side of the scale we find the Balmer lines of hydrogen disappearing at the Ob stage. This is an effect of complete ionisation. We have, therefore, at the stage

Ob ..... Complete ionisation of H.....  $22,000^\circ \text{C.}$  (Table VI).

But if some day we can overcome the limitations imposed by the atmospheric absorbing layer, and examine stellar spectra up to  $1000 \text{ \AA.U.}$ , it is very probable that we shall get the Lyman lines ( $1s-mp$ ) even at the lowest stage at which a star begins its life,\* just like Calcium "g."

The disappearance of Balmer lines from a certain class therefore does not mean that hydrogen is absent from this class, but rather that the stimulus is not sufficiently great to bring out the lines lying within the range of observation.

The position of helium is quite similar. It cannot be identified by its  $1s-mp$  lines, but by the  $2p-md$  lines (*vide* Table VII). This can take place only when a sufficient proportion of He-atoms have been converted to the  $2p$  state. Owing to the higher value of ionisation-potential of helium, this takes place, as Table II shows, at a much higher stage than that of hydrogen, viz., at the Ao stage. We have, therefore, at the stage

Ao .....  $2p$ -orbits of He just appearing .....  $T = 12,000^\circ \text{K.}$

The helium lines are very persistent, as Table II shows. They occur faintly in the Ob and Oa classes, and even in the gaseous nebula† up to the Pd stage.

\* Provided, of course, the continuous spectrum from the stellar nucleus extends up to  $\lambda = 1000 \text{ \AA.U.}$ , and is not wholly absorbed by the stellar atmosphere itself.

† Harvard 'Annals,' vol. 91, p. 5.

Here the transition stages have not been satisfactorily worked out. Now a glance at Table IV shows that if we take the pressure 1 atm., helium does not become completely ionised even at a temperature of  $30000^{\circ}$ . For a pressure of  $10^{-1}$  atm., the temperature of complete ionisation is  $25000^{\circ}$  K.

The ionisation of helium becomes marked from the B2-stage, as is shown from the appearance of the 4686 line. According to Fowler, this is the  $3d-4f$  line of  $\text{He}^+$ , and according to our theory, this requires for its absorption, not only a rather greater stimulus than that which suffices for mere ionisation, but also a greater concentration of the  $\text{He}^+$ -atoms. We can, therefore, assign to the stage

B2A ... Ionisation of He considerably advanced ...  $T = 17,000^{\circ}$ .

I have sought in vain for satisfactory data for Mg, which can be detected by the  $2p-3d_j$  lines only (*vide* Table VII).  $\text{Mg}^+$  is detected by the line 4481, which, according to Fowler, has the series-combination  $3d-4f$ . A glance at Table II shows that, at the Go-stage, the ionisation of Mg has been considerably advanced, reaching its completion at the Oa-stage. We have, therefore, at the stage

Oa .....  $\text{Mg}^+$  Completely ionised .....  $T = 23,000^{\circ}$  K.

Unfortunately, we have no data of the exact stellar classes from which the Sodium,  $D_1$ , and  $D_2$  lines, the Sr line 4607, the Ba line 5543, and the Mg triplet 3838, 3832, 3829, the  $\text{Sr}^+$  4215, 4077, and Ba 4554, 4904, ... just disappear. If these were available, they would have served as good landmarks for determining the temperature of emission of the stellar atmospheres at their various stages of evolution. If these arguments are correct, we are not justified in speaking of a star as a Hydrogen, Helium, or Carbon star, thereby suggesting that these elements form the chief ingredients in the chemical composition of the star. The proper conclusion would be that under the stimulus prevailing in the star, the particular element or elements are excited to radiation of their characteristic lines, while other elements are either ionised, or the stimulus is too weak to excite the lines by which we can detect the elements. This strikes at the root of the prevailing conception of primordial elements.

Table VIII shows the above results at a glance.

A serious discrepancy is shown by hydrogen, which, as shown by the presence of the Balmer lines, is present even beyond the Oa-stage (*vide* Table II,  $\text{He}^+$ , 4860; we called it an  $\text{He}^+$  line there in anticipation of the arguments which follow). But modern spectroscopic work has shown that the lines represented by the Balmer formula  $\nu = N(1/2^2 - 1/m^2)$  cannot only be due to hydrogen, but may be due to  $\text{He}^+$  and to  $\text{Li}^{++}$ . If the

Table VIII.

Phenomena.	Stellar class.	Temperature.	Remarks.
Appearance of the K line .....	Mc	4,000 K	Beginning of the ionisation of Ca.
Disappearance of the "g" line.....	B8A	13,000	Ca completely ionised.
Appearance of $Mg^+$ 4481 .....	Go	7,000	Mg considerably ionised.
Disappearance of the K line .....	Oc	20,000	$Ca^+$ completely ionised.
$Mg^+$ 4481 disappears .....	Oa	23,000	$Mg^+$ completely ionised.
Appearance of 4686 .....	B2A	17,000	He considerably ionised.
Disappearance of 4471 .....	Oa	24,000	He completely ionised.
Appearance of Balmer lines .....	Mb	( $10^{-1}$ atm.) 4,500	Appearance of the $2p$ -orbits of H.
Appearance of He lines .....	Ao	12,000	Appearance of $2p$ -orbits of He.
Maximum absorption of hydrogen lines	Ao	12,000	Maximum concentration of $2p$ -orbits of H.
Maximum absorption of helium lines	B2A	17,000	Maximum concentration of $2p$ -orbits of He.
Disappearance of 4295 .....	B8A	14,000	$Sr^+$ completely ionised.
Disappearance of Balmer-hydrogen lines	Ob	( $10^{-1}$ atm.) 22,000	H completely ionised.
Disappearance of 4686 .....	Pe	25,000°– 30,000°	$He^+$ completely ionised.

lines be due to  $He^+$ , they should have the same intensity as the Pickering lines  $\nu = 4N[1/4^2 - 1/(2m+1^2)]$ , for they form the even members of the  $4f-mk$  series of  $He^+$ . Now, if we look back at Table II, we find that this is actually the case from the Oa- to the Oc-class, but in Od and Oe, while the Pickering lines are fading away, the Balmer lines are gaining in intensity.

This fact, taken along with the result that at 20,000° K,  $10^{-1}$  atm. pressure hydrogen is completely ionised, leads us to the conclusion. The Balmer lines due to hydrogen disappear from the Ob-class; those occurring in the Oa-, Ob-class, are due to  $He^+$ . In the Oc-, Od-, and Oe-class, there are blends of H and  $He^+$  lines, but below B2A they are entirely due to hydrogen.

The question can be settled by accurately measuring the wave-lengths of the Balmer lines in the different spectral classes, for, owing to slightly different values of N in the case of hydrogen and helium, the wave-lengths are slightly different, as the following Table shows:—\*

Hydrogen Lines.	$He^+$ Lines.
$\nu = N_H[1/2^2 - 1/m^2]$ ,	$\nu = 4N_{He}[1/4^2 - 1/(2m)^2]$ .
M = 1 H $\alpha$ , $\lambda = 6562\cdot8$ ,	M = 1, $\lambda = 6560\cdot1$ .
M = 2 H $\beta$ , $\lambda = 4861\cdot3$ ,	M = 2, $\lambda = 4859\cdot3$ .
M = 3 H $\gamma$ , $\lambda = 4340\cdot5$ ,	M = 3, $\lambda = 4338\cdot7$ .
M = 4 H $\delta$ , $\lambda = 4101\cdot7$ ,	M = 4, $\lambda = 4100\cdot0$ .

\* Fowler, "Bakerian Lecture," 'Phil. Trans.,' A, vol. 214; Paschen, 'Ann. d. Physik,' vol. 49.

The lines  $\nu = N[1/2^2 - 1/m^2]$  also occur in the highest class of gaseous nebulae, Pa, which is far higher up than the class from which  $\text{He}^+$  disappears. There is thus a certain anomaly attached to the Balmer lines.

#### 7. *Concluding Remarks.*

The work thus corroborates Russell's view that the continuous variation of stellar spectral types is mainly due to the varying values of the temperature of the stellar atmosphere, and the classification B, A, F, G, K, M, which has been adopted by the Harvard Astrophysicists, as the result of long years of study and observation, are therefore seen to acquire a new physical significance.

Some minor differences may be noted here. It appears that the temperatures assigned by Wilsing and Scheiner to stellar classes below Go are rather too low. Wilsing and Scheiner assign a temperature of  $5000^\circ \text{K.}$  to stars of the Go-class, of which the sun is a typical example. But Biscoe\* has shown in a comprehensive work that the black-body temperature of the sun is in the neighbourhood of  $7500^\circ \text{K.}$  Wilsing and Scheiner's value is therefore too low. The temperatures assigned to the K5, Ma, Md classes ( $3200^\circ$ ,  $3100^\circ$ ,  $2950^\circ \text{K.}$ ) are too close to each other to explain the large difference in the spectra of these types. Moreover, if these were the true temperatures, the dwarf stars of these classes would possess liquid or solid crusts consisting of carbon, tungsten, tantalum, and probably of some compounds.†

From the fact that  $\text{Ca}^+$  first comes out in considerable quantities in the Mc class, we are probably right in assigning to this class a temperature of  $4000^\circ \text{K.}$  But more work is required in the spectral classification of the red stars before we can come to any definite conclusion on this point.

Adams and Kohlschütter‡ have recently shown that there exists considerable difference in the spectra of the giant and the dwarf stars of the same spectral class, when the intensity of certain groups of lines are compared. It will be seen from Sections 2 and 3 that the nature of the spectra is decided not only by the temperature, but also by the concentration of atoms in the stellar atmosphere. Probably the mass of the star and the average density act differently on elements of different atomic weight, so

\* Biscoe, 'Astrophysical Journal,' vol. 46 (1917).

† The melting points of tungsten and tantalum are  $3800^\circ \text{K.}$  and  $3200^\circ \text{K.}$  Carbon is a volatile substance, *i.e.*, has its boiling point lower than the melting point. But Lummer claims to have succeeded in melting carbon by running the arc in an enclosed space under its own vapour pressure. He estimates the melting point to be  $4200^\circ \text{K.}$  under a pressure of 1 atm. of its own vapour.

‡ Adams, 'Communications from Mount Wilson Solar Observatory,' No. 23, 1916.

far as the concentration in the effective layer from which the absorption lines originate is concerned. The problem, however, awaits further investigation.

In spite of the uncertainty in choosing the proper concentration for a given element, it will be admitted from what has gone before that the temperature plays the leading rôle in determining the nature of the stellar spectrum. Too much importance must not be attached to the figures given, for the theory is only a first attempt for quantitatively estimating the physical processes taking place at high temperature. We have practically no laboratory data to guide us, but the stellar spectra may be regarded as unfolding to us, in an unbroken sequence, the physical processes succeeding each other as the temperature is continually varied from 3000° K. to 40,000° K.

In conclusion, it is my great pleasure to record my best thanks to Prof. A. Fowler for the interest he has taken in the work, and the many valuable items of information, advice, and criticism with which he has helped me. I also wish to express my thanks to Mr. S. K. Ghosh, M.Sc., of the Calcutta University, for much useful help in the preparation of this paper.

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*On the Catalytic Dehydrogenation of Alcohols.*

By ERIC KEIGHTLEY RIDEAL.

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In spite of the numerous industrial processes developed for the hydrogenation of various organic substances with the aid of catalytic materials, but little work has been accomplished on the determination of the mass action equilibrium constants of organic substances which undergo thermal dissociation. Thus in the dissociation of ethyl alcohol into acetaldehyde and hydrogen, or of isopropyl alcohol into acetone and hydrogen, two reactions widely employed, the dependence of the degree of the dissociation on the temperature is unknown. Sabatier ('*La Catalyse en Chimie Organique*') states (p. 82) that acetaldehyde is easily hydrogenated at 140° C. and acetone at a temperature of 115° to 125° C. utilising nickel as a catalytic agent.

At higher temperatures, however, 200° to 350° C., acetone is not hydrogenated to isopropyl alcohol, but methyl isobutylketone and diisobutylketone are